PATENT SPECIFICATION

(11) 1 500 868

1 500 868

(21) Application No. 21891/76 (22) Filed 26 May 1976
(31) Convention Application No. 7516515
(32) Filed 27 May 1975 in
(33) France (FR)
(44) Complete Specification published 15 Feb. 1978
(51) INT CL² C08F 10/00 2/34
(52) Index at acceptance
C3P 404 428 438 440 452 464 474 486 574 582 590 596 LA

(72) Inventors FRANCOIS CAUMARTIN and LASZLO HAVAS

(19)

(54) OLEFIN POLYMERIZATION IN A FLUIDIZED BED

(71) We, NAPHTACHIMIE, a French body corporate, of 203, rue du Faubourg Saint Honore, 75008 Paris, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention is concerned with polymerization of olefins in a fluidized bed to produce solid polymers or copolymers having a molecular weight generally higher than 50,000. The method of the invention is particularly applicable to the polymerization of ethylene alone or mixed with other olefins.

It is known that ethylene contained in a gaseous mixture can be polymerized in a reaction vessel in which the solid polymer in course of formation is kept in the fluidized state by means of an upward stream of the gaseous mixture. At the outlet of the reaction vessel the gaseous mixture is generally cooled before being recycled into the reaction vessel with a further quantity of ethylene. Polymerization is carried out in the presence of a catalytic system comprising a catalyst formed by a compound of a transition metal, such as a solid compound of trivalent titanium, and a co-catalyst constituted by an organic compound of a light metal, generally a liquid organo-aluminium compound.

In order to obtain an active catalytic system, these two components are contacted either before they are introduced into the polymerization reaction vessel or within this vessel. This second technique is particularly recommended when the catalyst is constituted by a solid, since it is difficult to mix such a catalyst with a liquid co-catalyst. However, in order to bring the co-catalyst rapidly into contact with the catalyst, the direct introduction of a liquid co-catalyst into the polymerization reaction vessel has only been envisaged as a practical step in the case of co-catalysts that are sufficiently volatile to vaporize rapidly in the gaseous mixture present in the reaction vessel and therefore to enter into contact with the catalyst. For this reason diethyl aluminium chloride is one of the co-catalysts most frequently recommended. However, the use of co-catalysts of this type is accompanied by difficulties inherent in the volatility of these compounds which are in fact removed from the reaction vessel by entrainment in the gaseous mixture as it leaves the vessel, and this results in rapid reduction in the rate of polymerization. The co-catalysts removed from the reaction vessel are furthermore likely to condense in the cold portions of the circulatory duct through which the gases pass and are thus likely to cause polymerization to take place outside the reaction vessel when they are in contact with fine particles of the catalyst, which may likewise be entrained by the gaseous mixture.

The present invention is based on the discovery that it is possible to polymerize olefins in a fluidized bed in contact with solid catalysts and low-volatility liquid co-catalysts, the co-catalyst being introduced separately from the catalyst into the polymerization reaction vessel on a carrier constituted by an inert porous powder impregnated with the co-catalyst.

The invention provides a method of producing polymers having a mean molecular weight higher than 50,000 from olefins of the formula

$$CH_2=CHR,$$

where R is a hydrogen atom or an alkyl radical having a maximum of 8 carbon atoms, in a polymerization reaction vessel in which the polymer in course of formation is kept in a fluidized state by an upward stream of a gaseous mixture containing the olefin or olefins to be polymerized, in the presence of a catalytic system incorporating a catalyst constituted by a solid containing

at least one compound of a transition metal from sub-group IVa, Va or VIa of the Mendeleeff periodic table, and a co-catalyst constituted by at least one organo-metallic compound of a metal from group II or III of the periodic table, the co-catalyst being liquid under the polymerization conditions, having a vapour pressure lower than 1 mm of mercury at 80°C, and being introduced into the polymerization reaction vessel separately from the catalyst and on a carrier constituted by a porous powder that is stable under the polymerization conditions and does not react with the olefin or the components of the catalystic system and that is impregnated with the co-catalyst.

The method of the invention is preferably applied to the production of polyethylene or to the production of copolymers of ethylene and other olefins of the formula

$$CH_2{=}CHR$$

mentioned above.

The co-catalyst used in the method of the invention is preferably a liquid organo-aluminium compound having the general formula

$$AlR'_xY_{3-x},$$

where R' represents an alkyl group having 4 to 20 carbon atoms, Y an atom of hydrogen or a halogen, preferably chlorine, and x a whole number or a fraction having any value of from 1 to 3. The co-catalyst is advantageously introduced into the reaction vessel in quantities such that the atomic ratio, i.e. the ratio of the aluminium of the co-catalyst to the transition metals from the sub-groups IVa, Va and VIa forming the catalyst, is in the range 0.1:1 to 50:1.

The porous powder on which the co-catalyst is carried is preferably constituted by solid particles the mean diameter of which is between 10 microns and 1 mm and the porosity of which is such that the proportion of voids is at least 10%.

The porous powder may be a solid inorganic substance that is substantially inert under polymerization conditions and does not react either with the olefins or the components of the catalystic system; the porous powder may for example be constituted by particles of dehydrated alumina, silica, silicates of metals such as aluminium and/or magnesium, or a calcium carbonate and/or magnesium carbonate. Preferably however the porous powder is a solid organic substance that is stable under the polymerization conditions. Polyolefin powders are for example particularly suitable; in particular they may be constituted by the polymer prepared during the method of the invention. Since the co-catalyst reacts with water, it is preferred to use a porous powder that is substantially dry so as to avoid losses of co-catalyst.

The porous powder may be impregnated with co-catalyst by mechanical mixing, for example, in a mixing machine of the screw or blade type, or by fluidization with the aid of a gas until a ready-flowing powder of dry appearance is obtained. Depending upon their nature, the porous powders can be impregnated with greatly varying quantities of co-catalyst, and the proportion by weight of co-catalyst in relation to the powder may vary for example from 0.5 to 5%; this proportion is not however a critical feature of the invention.

As already mentioned above, the catalytic system also includes a catalyst containing a solid compound of a transition metal from sub-group IVa, Va or VIa of the periodic table. These transition metals include titanium, vanadium, chromium, zirconium, niobium, molybdenum, hafnium, tantalum and tungsten.

The transition metal compound may in particular be a solid compound of tervalent titanium having the general formula

$$TiX_{3-m}(OR'')_m,$$

where X represents an atom of halogen, generally chlorine, R'' an alkyl radical containing from 2 to 8 carbon atoms, and m a whole number or a fraction of any value from 0 to 3. These tervalent titanium compounds are currently obtained by the reduction, by means of organo-aluminium compounds for example, of quadrivalent titanium compounds of the formula

$$TiX_{4-n}(OR'')_n,$$

where X and R'' have the same meanings as above and n is a whole number or fraction of any value from 0 to 4. The compounds of the formula

$$TiX_{4-n}(OR'')_n$$

in which n is other than 0 and 4, can be obtained from calculated quantities of a titanium tetrahalogenide of the formula TiX_4 and of an alkyl tetratitanate of the formula

$$Ti(OR'')_4,$$

by a functional interexchange reaction which may be expressed as follows:

$$\frac{4-n}{4}TiX_4+\frac{n}{4}Ti(OR'')_4\rightarrow Ti\,X_{4-n}(OR'')_n$$

The transition metal compound is

preferably constituted by a solid mixed compound of transition metal and magnesium, and this compound can be obtained for example by reaction a quadrivalent titanium compound with an organo-magnesium compound. The mixed compounds of this type in fact generally display great catalytic activity in the polymerization of olefins.

The catalyst may be constituted by a solid compound of a transition metal, such as one of the titanium compounds mentioned above, or it may be associated with a solid carrier constituted for example by granules of silica, alumina or magnesia, on which the transition metal compound is deposited or fixed. The catalyst may also be constituted by a prepolymer obtained by preliminary polymerization of one or more olefins in an inert liquid such as an aliphatic hydrocarbon and in the presence of a transition metal compound, such as that defined above, and of a co-catalyst, such as an organo-aluminium compound. Prepolymerization is arrested after the formation of a moderate quantityof polymer, usually from 1 to 500 g per milliatom-gramme of transition metal of the catalyst. After separation of the liquid in which the prepolymer has been prepared, the prepolymer, in which the transition metal compound remains included, may then be used directly as a solid having catalytic activity. It is however preferable, before using the prepolymer in the method of the invention, to subject it to one or more extractions by means of a solvent such as an aliphatic hydrocarbon so as to create porosity within the granules of the prepolymer. This porosity makes it easier for the olefins to reach the catalytic sites.

The polymer present in the polymerization reaction vessel is maintained in the fluidized state in an upward stream of the gaseous mixture containing the olefin or olefins to be polymerized and preferably hydrogen in proportions which, in volume, may be as high as 90% of that of the gaseous mixture. The latter is advantageously constituted by the gaseous mixture that issues from the reaction vessel, which is recycled, together with a quantity of the olefin or olefins to be polymerized, which quantity is introduced into the circulatory system in which the reaction takes place.

The speed of upward travel to be imparted to the gaseous mixture in order to keep the polymer that is present in the reaction vessel in the fluidized state will depend upon the physicl parameters of the polymer and the gaseous mixture, the main parameters being the particle-size of the polymer, the specific mass of the polymer and the viscosity and specific gravity of the gaseous mixture; speeds of upward travel of the order of several decimetres per second are the most usual.

In the reaction vessel, the temperature is maintained at a level high enough to ensure that polymerization proceeds rapidly, but this temperature should not be too close to the softening temperature of the polymer so as to avoid the formation of the polymer agglomerates. In the production of polyethylene, the temperature is generally in the range 30 to 115°C. The temperature is maintained at the required level in the reaction vessel, preferably by cooling the gaseous mixture issuing from the reaction vessel, thus enabling the heat produced during polymerization to be removed.

The partial pressure to which the olefin(s) being polymerized is (are) subjected will depend upon the nature of the olefins and upon the temperature obtaining in the apparatus and will be such as to prevent the olefins from liquefying in the coldest portion of the circulatory system. In practice this risk only exists with olefins other than ethylene; when ethylene is used as the starting material for polymerization, temperatures are maintained at levels higher than the critical temperature for ethylene, i.e. near 10°C, the total pressure then usually being in the range 1 to 40 bars.

The gaseous mixture is in contact with the catalyst present in the reaction vessel during only a limited period, generally less than a few dozen seconds. Thus, only a fraction of the olefin or olefins introduced into the reaction vessel is polymerized therein, and consequently it is in practice necessary to recycle into the reaction vessel the gaseous mixture that issues from it. To prevent the gaseous mixture from carrying away particles of polymer or catalyst at the outlet of the reaction vessel, the latter may for example be provided at its top with what is known as a tranquillization chamber having a cross-section greater than that of the reaction vessel; in this chamber the speed of upward travel of the gaseous mixture is lower than in the reaction vessel and this enables the entrained polymer particles or catalyst particles to drop back into the reaction vessel. The particles entrained by the gaseous mixture may also be separated in a cyclone and may be returned to the reaction vessel and preferably to the lower part thereof. Since the polymerization of olefins causes the release of heat, it is necessary to eliminate the heat produced so as to maintain a constant temperature in the reaction vessel; removal of this heat is preferably achieved by causing the gaseous mixture that is to be recycled to circulate in a heat-exchanger located outside the reaction vessel.

The method of polymerizing olefins in accordance with the invention may also be

used in several fluidized-bed reaction vessels arranged in series. In this case only part of the polymerization is carried out in each reaction vessel, and the polymer in course of formation circulates from the first reaction vessel to the last. In a modified arrangement, certain reaction vessels may be arranged in parallel so that the polymer in course of formation and issuing from one reaction vessel supplies two or more secondary reaction vessels.

The finished polymer may be discharged from the reaction vessel in which it is produced by means of various mechanical systems. One discharge means involves providing the lower part of this reaction vessel with a closable orifice communicating with an enclosure in which a lower pressure obtains than in the reaction vessel. Uncovering of the orifice during a predetermined period enables the required quantity of polymer to be introduced into this enclosure. When the opening has been closed again, all that is then required is to connect the enclosure with the exterior in order to collect the polymer.

The method of the invention is preferably used in such a way that the operating conditions of the reactor or reactors are substantially constant. This mode of operation may be achieved in practice by circulating, in each reaction vessel, a gaseous mixture having substantially constant properties and mainly constituted by the recycled gaseous mixture.

It has been observed that, despite the low volatility of the co-catalyst used in the method of the invention, polymerization proceeds in a satisfactory manner. This is unexpected since the co-catalyst situated within the porous particles of the carrier is not in direct contact with the catalyst. This result runs counter to the theories at present put forward on this type of polymerization. Apart from the advantage obtained by the use of low-volatility co-catalysts that are not in danger of being carried over to the polymerization reaction vessels through the exterior gas-circulating system, the invention can also reduce the risk of localized overheating in the polymerization reaction vessels. This advantage is particularly desirable when use is made of catalysts having high activity such as the mixed catalysts based on magnesium and transition metals mentioned above.

EXAMPLE 1

a) Preparation of a catalyst

First, *n*-butyl magnesium chloride was prepared in a 5-litre stainless steel reaction vessel provided with mechanical stirring means, a reflux refrigerant and a heating or cooling means, by circulating a fluid in a jacket. 21.9 g (900 milliatom-g) of powdered magnesium, 600 ml of dry *n*-heptane, 83.3 g (900 millimoles) of *n*-butyl chloride, and one iodine crystal were then introduced into the reaction vessel in a nitrogen atmosphere and at ambient temperature (25°C). The reaction medium was heated to 75°C, and the reaction was started up and was continued under these conditions for 2 hours. When the reaction was complete, a suspension of 900 millimoles of *n*-butyl magnesium chloride in *n*-heptane was obtained.

Still in a nitrogen atmosphere, the suspension of *n*-butyl magnesium chloride was heated at 75°C, and over a period of 2 hours a solution of 57 g (300 millimoles) of titanium tetrachloride and 83.3 g (900 millimoles) of *n*-butyl chloride in 350 ml of *n*-heptane was gradually introduced by means of a metering pump. After introduction of the solution had been completed, the reaction medium was maintained at 75°C for 1 hour, stirring of the mixture taking place.

The brown-black precipitate obtained was washed several times with *n*-heptane. The composition of the dry catalyst by weight was Ti, 8.3%; Mg, 18.2%; Cl, 73.5%.

b) Polymerization of ethylene

The operation was carried out in a fluidized bed reaction vessel constituted by a 15-cm-diameter steel tube provided at the top with a tranqillization chamber; the total height of the reaction vessel was 1 m. The fluidizing grid was constituted by a plate made of fritted stainless steel. The reaction vessel was kept at a constant temperature by means of a jacket within which circulated a refrigerating liquid.

The reaction vessel contained 1 kg of a polyethylene powder which had been impregnated beforehand with 30 g of tri-*n*-octyl aluminium, the vapour tension of which at 80°C was considerably less than 1 mm of mercury (not measurable). The powder was kept in the fluidized state by an upward stream of gas moving at a speed of 15 cm/sec; this gas was constituted by a mixture of 50% by volume of ethylene and 50% by volume of hydrogen. 10 g of the catalyst prepared in the manner described above at a) was introduced into the reaction vessel. After 6 hours' operation at 80°C at atmospheric pressure it was found that 610 g of polymer had formed, the weight of the powder being 1650 g. During the test no lumping or formation of polymer agglomerates occurred.

EXAMPLE 2

By way of comparison, the test described in Example 1 was repeated, but the tri-*n*-octyl aluminium was replaced by an equivalent molecular quantity of diethyl

aluminium chloride, the vapour tension of which at 80°C was 9 mm of mercury. Polymerization was observed to start up, but it slowed down rapidly and stopped after 2 hours. It was found that only 70 g of polymer had been formed.

EXAMPLE 3

The same operating conditions as in Example 1 were used, but polymerization proceeded at a total pressure of 20 bars, and only 20 g of tri-*n*-octyl aluminium were used. After polymerizing for 2 hours, it was found that 1900 g of polyethylene were formed.

EXAMPLE 4

By way of comparison, the test described in Example 3 was repeated, but the tri-*n*-octyl aluminium was replaced by an equivalent molecular quantity of diethyl aluminium chloride. After 2 hours it was found that polymerization had stopped and that 350 g of polymer had formed, part of this being constituted by agglomerates. The presence of encrustations adhering to the walls was also observed.

EXAMPLE 5

The same operating conditions as in Example 3 were used, but the tri-*n*-octyl aluminium was replaced by an equivalent molecular quantity of tri-*n*-tetradecyl aluminium, the vapour tension of which at 80°C was considerably less than 1 mm of mercury (not measurable).

After 2 hours of polymerization, it was found that 1800 g of polyethylene had formed.

EXAMPLE 6

The test described in Example 3 was repeated, but using a gaseous mixture made up of 20% by volume of ethylene and 80% by volume of hydrogen, at a total pressure of 10 bars. After 10 hours of polymerization it was found that 500 g of polymer had formed.

WHAT WE CLAIM IS:—

1. A method of producing polymers having a mean molecular weight higher than 50,000 from olefins of the formula

$$CH_2{=}CHR,$$

where R is a hydrogen atom or an alkyl radical having a maximum of 8 carbon atoms, in a polymerization reaction vessel in which the polymer in course of formation is kept in a fluidized state by an upward stream of a gaseous mixture containing the olefin or olefins to be polymerized, in the presence of a catalytic system incorporating a catalyst constituted by a solid containing at least one compound of a transition metal from sub-group IVa, Va or VIa of the Mendeleeff periodic table, and a co-catalyst constituted by at least one organo-metallic compound of a metal from group II or III of the periodic table, the co-catalyst being liquid under the polymerization conditions, having a vapour pressure lower than 1 mm of mercury at 80°C, and being introduced into the polymerization reaction vessel separately from the catalyst and on a carrier constituted by a porous powder that is stable under the polymerization conditions and does not react with the olefin or the components of the catalytic system and that is impregnated with the co-catalyst.

2. A method according to Claim 1, in which the co-catalyst is constituted by one or more liquid organo-aluminium compounds of the general formula

$$AlR'_xY_{3-x},$$

where R′ represents an alkyl group having 4 to 20 carbon atoms, Y an atom of hydrogen or a halogen, and x a number having any value of from 1 to 3, the co-catalyst being used in a quantity such that the atomic ratio, i.e. the ratio of the aluminium of the co-catalyst to the transition metal(s) of the catalyst, is in the range 0.1 to 50.

3. A method according to Claim 2, in which Y is a chlorine atom.

4. A method according to any one of Claims 1 to 3, in which the porous powder carrying the co-catalyst is constituted by solid particles, the mean diameter of which is in the range 10 microns to 1 mm and the porosity of which is such that the proportion of voids is at least 10%.

5. A method according to any one of Claims 1—4 in which the porous powder carrying the co-catalyst is a solid inorganic substance.

6. A method according to Claim 5 in which the solid inorganic substance is dehydrated alumina, silica, an aluminium silicate and/or a magnesium silicate, or calcium carbonate and/or magnesium carbonate.

7. A method according to any one of Claims 1—4 in which the porous powder carrying the co-catalyst is a polymer powder.

8. A method according to Claim 7 in which the polymer powder is a polyolefin powder.

9. A method according to any one of Claims 1—8 in which the catalyst is a titanium compound.

10. A method according to any one of Claims 1—9 in which the polymerized olefin

is ethylene, polymerization being carried out by starting with a gaseous mixture containing up to 90% by volume of hydrogen, the pressure being in the range 1 to 40 bars and the temperature in the range 30 to 115°C.

11. A method according to Claim 1, substantially as hereinbefore described in Examples 1, 3, 5 and 6.

12. Polymers prepared by a method according to any one of the preceding claims.

For the Applicants,
D. YOUNG & CO.,
Chartered Patent Agents,
9 and 10, Staple Inn,
London, WC1V 7RD.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1978
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.